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ULTRASONIC VELOCITY IN SOME AQUEOUS SOLUTIONS OF ELECTROLYTES

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ABSTRACT. The variation of ultrasonic velocity, adiabatic compressibility, apparent molal compressibility and molar sound velocity with concentration is studied in eleven electrolyte solutions. The results are interpreted in the light of Debye-Huckel's theory of electrolytes. The hydration numbers are estimated for all the electrolytes and compared with the data obtained by other methods. Non-linear variations of molar sound velocity with molar concentration observed in some cases is explained in terms of molecular association and ionic solvation.

1. INTRODUCTION

Ultrasonic velocity measurements in electrolytic solutions are of considerable importance as they enable us to test the validity of the several theories of electrolyte solutions. Besides it has been possible to estimate the number of water molecules attached to the ions in solution known as hydration number. Following the theory of Debye-Huckel, Gucker (1933) has derived certain limiting laws for the apparent molal compressibility and interpreted his experimental data in the light of this theory. Subsequently Bachem (1936), Scot, Obenhaus and Wilson (1934), Krishnamurty (1950), Rao and Rao (1958) studied the apparent molal compressibilities in several solutions of electrolytes of different valence types and reported deviations from the limiting laws. While studying variations of ultrasonic velocities in solutions of electrolytes certain unusual features like decrease of velocity with increase of concentration have also been reported by some investigators in a few electrolytes namely, potassium iodide, lead nitrate, lead acetate and uranyl acetate. Very recently, Marks (1960) has calculated the hydration numbers for salts of alkali metals investigated by him.

As very little work has been done particularly on the estimation of hydration numbers and molar sound velocities in the case of solutions of electrolytes, the authors have taken up this investigation by taking measurements for about eleven new electrolytes.

2. RESULTS

Aqueous solutions of the following salts are studied.

1. Lithium acetate.
2. Sodium acetate.
3. Potassium acetate.
4. Cobaltous acetate.
5. Cadmium acetate
6. Cadmium chloride.
7. Cadmium Bromide
8. Strontium Bromide.
9. Barium bromide.
10. Cadmium Iodide.
11. Zinc Iodide.

The salts used are of either E. Merck or B. D. H. Solutions of different concentrations are prepared and the ultrasonic velocities are determined by a fixed path variable frequency interferometer accurate to ± 1 *m*/sec The densities (ρ) are determined by specific gravity bottle using a Bunge balance accurate to 1 mgm.

The values of adiabatic compressibility β and apparent molal compressibility $\phi(k_2)$ are calculated by using the relations

$$\beta = \frac{1}{\rho V^2}, \quad \phi(k_2) = \frac{\beta \times 1000}{C'} - \frac{\beta_1}{d_1}\left(\frac{1000d}{C'} - M\right)$$

Where β_1 is the adiabatic compressibility of the solvent, C' = Molar concentration and M = the molecular weight of the solute.

The variation of ultrasonic velocity, adiabatic compressibility and apparent molal compressibility with concentration for all the eleven salts investigated is shown graphically in Figs. 1 to 6.

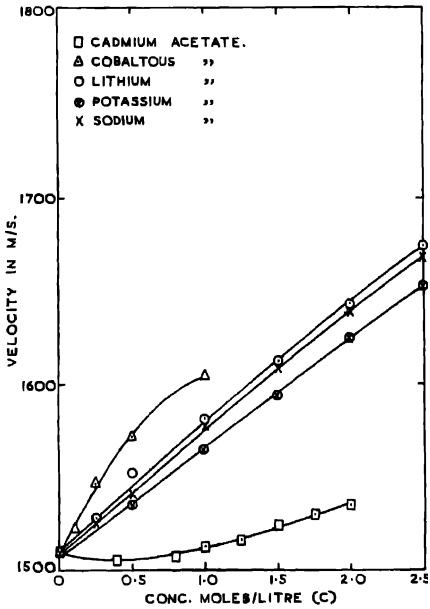

FIG. 1. Variation of ultrasonic velocity with concentration of the electrolyte.

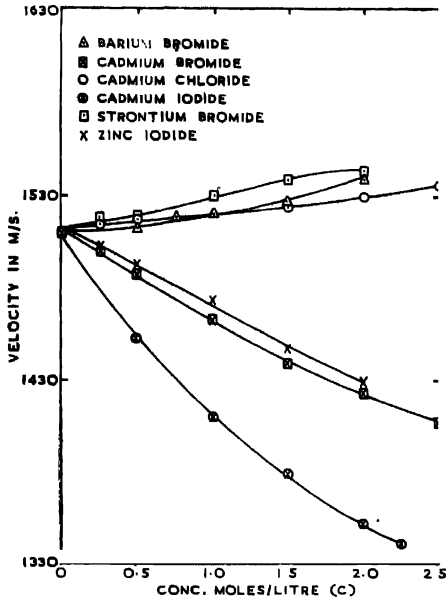

FIG 2 Variation of ultrasonic velocity with concentration of the electrolyte.

VARIATION OF ULTRASONIC VELOCITY AND ADIABATIC COMPRESSIBILITY WITH CONCENTRATION

It can be seen from Figs. 1 and 2 that in almost all the salts studied, the velocity is found to increase with concentration except in the cases of zinc iodide, cadmium bromide and iodide. Cadmium acetate solution showed a slight decrease in velocity initially and then showed gradual increase with concentration almost linearly. Although the anomalies of decrease of velocity with increase of concentration are noticed for these four salts, the adiabatic compressibility always showed the normal decrease with increase of concentration as can be seen in Figs. 3 and 4. The non-linear variation of velocity with concentration in the case of cobalt acetate is similar to the non-linear variation exhibited by some ferrous salts. A comparative study of the behaviour in the case of cadmium halides shows that the gradient of velocity-concentration graph decreases progressively from cadmium chloride to iodide. In a similar manner the velocities for barium bromide solutions are lower than those of barium chloride solutions studied by

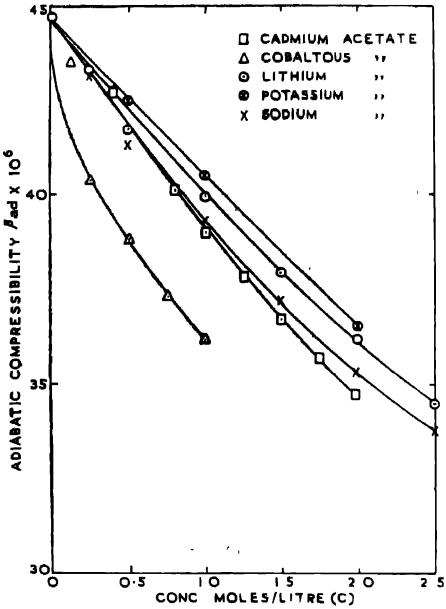

FIG. 3. Variation of adiabatic compressibility with concentration of the electrolyte.

Bachem (1936). It appears from these observations that for a fixed positive radical increase of atomic weight of the negative radical in the halogen group decreases the ultrasonic velocity. This is also borne out by data available for alkali halides studied by earlier works (Bachem, 1936; Krishnamurty, 1950 and Wada *et al.*, 1950).

It may also be noted that solutions of all the iodides studied so far show a decrease of velocity with concentration at first and later on show an increase in some cases.

The compressibility is always found to decrease with increase of concentration following closely the equation.,

$$\beta = \beta_1 + AC + BC^{3/2}$$

given by Gücker (1933).

From a systematic study of a series of aqueous solutions of some sulphates Marks (1944) has drawn the important conclusion that for a fixed anion the com-

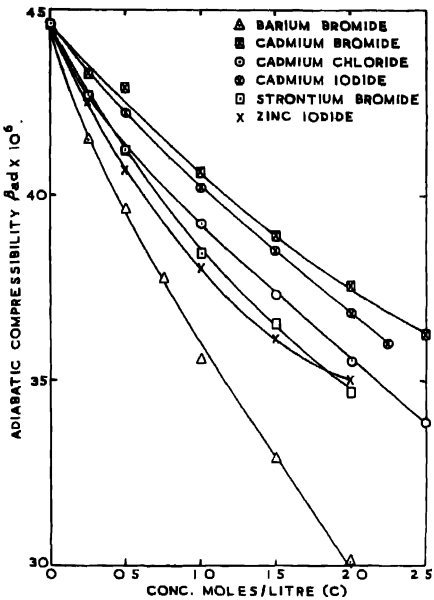

FIG. 4. Variation of adiabatic compressibility with concentration of the electrolyte.

pressibility at a particular concentration decreases with increasing ionic radius of the cation. Here an attempt is made to interpret the results of this investigation in the light of this rule. For this purpose the data available in literature are also utilised. The compressibility data for different electrolyte solutions at a fixed concentration either 0.5 M to 1.0 M are presented in Table I.

Comparing the sodium-flouride, chloride and nitrate solutions with the corresponding potassium salt solutions for the same concentration it is seen that the compressibility of the potassium salt solutions is always less. This may be attributed to the higher radius of K^+ ion compared to Na^+ ion. Comparing the adiabatic compressibilities of 1M solutions of $MgCl_2$, $CaCl_2$, $CdCl_2$ it is seen that $CdCl_2$ and $CaCl_2$ obey the above rule while $MgCl_2$ shows deviation from it This deviation may be due to the partial hydrolysis of magnesium chloride into magnesium hydroxide. All the three bromide solutions studied follow this rule quite well. The two iodides of zinc and cadmium show deviation from this rule. Similar deviations are noticed in the case of nitrates and sulphates of Fe, Co, Ni which hydrolyse in aqueous solutions. It is obvious that the effect of water of

TABLE I

Salt	Formula		Conc. Moles/ litre	$\beta \times 10^{12}$ Cm^2/dyne	Ionic radius of the Å catio
Sodium fluoride	NaF	(1-1)	0 5	42.14	0.95
Potassium fluoride	KF	(1-1)	0.5	39.43	1.33
Sodium chloride	NaCl	(1-1)	1.0	38.02	0.95
Potassium chloride	KCl	(1-1)	1.0	36.46	1.33
Magnesium chloride	$MgCl_2$	(2-1)	1.0	35 70	0.65
Calcium chloride	$CaCl_2$	(2-1)	1.0	36.50	0.99
Cadmium chloride	$CdCl_2$	(2-1)	1.0	39.37	0 97
Sodium nitrate	$NaNO_3$	(1-1)	0.5	41.73	0.95
Potassium nitrate	KNO_3	(1-1)	0 5	41 03	1 33
Strontium nitrate	$Sr(NO_3)_2$	(2-1)	0.3	41 01	1 13
Barium nitrate	$Ba(NO_3)_2$	(2-1)	0.3	40 52	1 35
Nickel nitrate	$Ni(NO_3)_2$	(2-1)	0 3	41 80	0 69
Barium bromide	$BaBr_2$	(2-1)	1 0	35.96	1 35
Strontium bromide	$SrBr_2$	(2-1)	1.0	38.59	1.13
Cadmium bromide	$CdBr_2$	(2-1)	1 0	39.88	0.97
Zinc Iodide	ZnI_2	(2-1)	1.0	37 27	0 74
Cadmium iodide	CdI_2	(2-1)	1.0	39.46	0 97
Magnesium sulphate	$MgSO_4$	(2-2)	0.5	36 77	0.65
Zinc sulphate	$ZnSO_4$	(2-2)	0 5	36 34	0 74
Iron sulphate	$FeSO_4$	(2-2)	0.5	38 80	0.75
Lithium acetate	$Li(CH_3COO)\ 2H_2O$	(1-1)	1 0	39 15	0.60
Sodium acetate	$Na(CH_3COO)3H_2O$	(1-1)	1.0	38.54	0.95
Potassium acetate	$K(CH_3COO)$	(1-1)	1.0	39.77	1.33
Cadmium acetate	$Cd(CH_3COO)_22H_2O$	(2-1)	1.0	38.32	0.97
Cobaltous acetate	$Co(CH_3COO)_24H_2O$	(2-1)	1.0	35 52	0 72

hydration is to decrease the compressibility of the solution —If we however compare the three salts lithium, sodium and cadmium acetates having nearly the same number of molecules of water of crystallization, it will be seen that the compressibility decrease from lithium to cadmium where as the ionic radius increases from Li^+ to Cd^{++} progressively. The deviation from this rule observed in the case of cobaltous acetate may be partly due to hydrolysis and partly due to the large

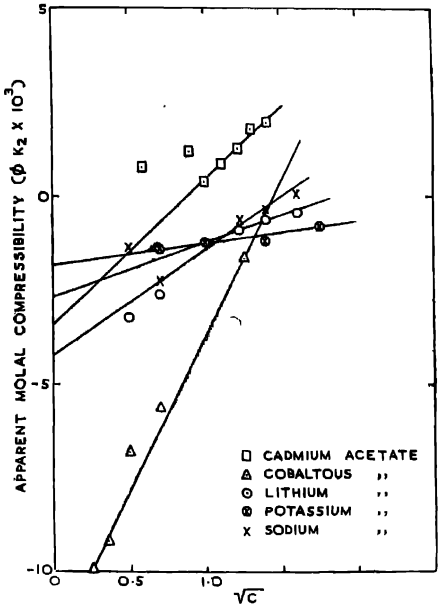

FIG 5. Relation between apparent molal compressibility and squareroot of concentration.

number of molecules of water of crystallisation, the high value of compressibility for solutions of potassium acetate compared to others inspite of its large ionic radius of 1.33 may be attributed to the lack of water of crystallisation.

APPARENT MOLAL COMPRESSIBILITIES AND ESTIMATION OF HYDRATION NUMBERS

It can be seen from Figs. 5 and 6 that the apparent molal compressibility $\phi(k_2)$ varies almost linearly with square root of concentration in all cases except cadmium salts for which deviations are noticed particularly at lower concentrations. The values of $\phi(k_2)$ for most of the salt solutions are generally negative and there are very few cases for which positive values are reported. In this investigation positive values of $\phi(k_2)$ are observed for the case of cadmium acetate, bromide and Iodide and strontium bromide solutions. The values of the gradients $\frac{\partial\phi(k_2)}{\partial\sqrt{c}}$ are determined and presented in Table II along with the theoretically computed values.

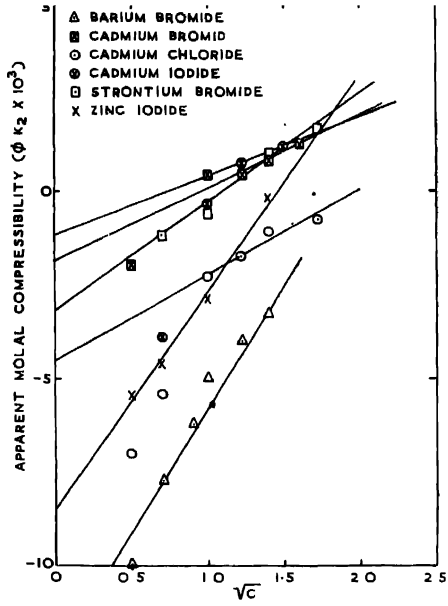

FIG. 6. Relation between apparent molal compressibility and square root of concentration.

TABLE II

Salt	Type of Electrolyte	$(\varepsilon r_i z_i^2)^{3/2}$	$\{\partial\phi(k_2)/\partial c^{1/2}\}$		(K_2) $\times 10^3$ $c \to 0$	Hydration number
			10^{10} C.G.S. Theoretical	10^4 Expt.		
Lithium acetate $2H_2O$	1-1	2 828	6.3	29.50	−2.90	3 60
Sodium acetate $3H_2O$	1-1	2 828	6.3	23.00	−3.55	4.40
Potassium acetate	1-1	2 828	6.3	12 50	−3.30	4.20
Cadmium acetate $2H_2O$	2-1	14 700	32.6	40.00	+3.50	4.40
Cabaltous acetate $4H_2O$	2-1	14 700	32.6	110 00	−22.90	28.50
Barium bromide	2-1	14.700	32.6	67.44	−12.20	15.40
Strontium bromide	2-1	14.770	32.6	15.80	−3.66	4.50
Cadmium bromide	2-1	14.700	32.6	43.00	−0.80	—
Cadmium iodide	2-1	14.700	32.6	34.00	−0.38	—
Cadmium chloride	2-1	14.700	32.6	26.66	−5.00	6.20
Zinc iodide	2-1	14.700	32.6	62.10	−9.18	1.40

In the (1– 1) type electrolytes studied the slopes of almost all the solutions show deviations from the theoretical values but it is found that the experimental values are always higher. There is a fairly good agreement between experimental and theoretical values in the case of the (2—1) type salts cadmium acetate, bromide and iodide although these solutions showed unusual behaviour in other physical properties. Although strontium bromide and cadmium chloride belong to (2—1) valence type, their gradients are even smaller than the theoretical values of the (1—1) type electrolyte solutions. In general, it may be concluded from the above study of the apparent molal compressibilities that Gucker's limiting law is only in qualitative agreement with the experimental values.

It is well known that the water molecules in the immediate neighbourhood of ions in an electrolyte solution are intimately bound to the ions. This process is known as hydration. The first layer of water molecules attached to the ion is known as primary water of hydration Estimation of primary hydration numbers of ions is now possible by several methods based on diffusion, ionic mobilities, activity coefficients etc. Hydration numbers can also be estimated from a study of apparent molal compressibility on the assumption that the ion as well as the primary water of hydration are incompressible compared to the free solvent molecules. Wada and Shimbo (1950) have given the following relation from which the hydration number can be calculated

$$\lim_{c\to 0} \phi(k_2) = -\beta_1 V_h$$

V_h is the volume of primary water of hydration for more of the electrolyte. The limiting value $\lim_{c\to 0} \phi(k_2)$ can be obtained by extrapolating $\phi(k_2)$ versus $\sqrt{c}$ graph to zero concentration. Using the experimental values of $\lim_{c\to 0} \phi(k_2)$ and β_1 the values of V_h are estimated. By making the further assumption that the molar volume of the solvent molecules in the primary hydration sheath is the same as that of the pure solvent, the combined primary hydration number for the electrolyte is obtained by dividing V_h by the molar volume of water. The experimental values thus obtained for all the electrolytes investigated are presented in the last column in Table II. The values of hydration numbers of lithium, sodium and potassium acetates are nearly of the same order of magnitude as the values 4, 5 and 5, for the ions Le^+, Na^+ and K^+ respectively available in literature (Bell, 1958). This leads to the conclusion that the contribution due to the acetate radical is very low. The low values of 4.4 obtained for cadmium acetate shows that the hydration number of Cd^{++} ion is of the same order as Na^+ or K^+ ions although it is doubly ionised. Assuming the contribution of Cl^- ion to combined hydration number as unity as obtained from activity coefficients method, it will be seen that the data for $CdCl_2$ leads to the same value of about 4 for the primary hydration number

of Cd^{++} ion. The abnormally low values of hydration number obtained for $CdBr_2$ and CdI_2 may be attributed to the anomalous variation of ultrasonic velocity with concentration and the non-linear nature of $\phi(k_2)$ versus $c^{\frac{1}{2}}$ plot. Cobaltous acetate gives an abnormally high value of 28.5 for the hydration number part of which may be due to hydrolysis. Taking the value for bromine as one, the hydration number for Sr comes out to be approximately 4 which is of the same order as Na^+ or K^+ ions. Similarly, the values obtained for Ba^{++} and Zn^{++} ions are 13 and 9 respectively.

MOLAR SOUND VELOCITY AND ASSOCIATION

Rao (1940) has shown that the molar sound velocity R given by $\frac{M}{\rho}(V)^{1/3}$ is independent of temperature for non-associated liquids. For associated liquids like water and alcohol, R varies appreciably with temperature and Weissler has utilised this variation for studying the change of relative association with temperature. It is well known that in the case of ideal solutions where there is no association or complex formation, the R value for the solution estimated by using the relation

$$R = \frac{\bar{M}}{\rho}(V)^{1/3}$$

where $$\bar{M} = \frac{n_1 M_1 + n_2 M_2}{n_1 + n_2}, \qquad C_m = \frac{n_1}{n_1 + n_2}$$

varies linearly with molar concentration of the solute C_m from the value of R for the solvent to that of the solute. The theoretically computed values of R from the known molar sound velocity increments for the atoms may be taken to be equal to the values for the ideal solution. The R values for the various solutions investigated are computed and it is found that the R variation with molar fraction is nearly linear in all cases except cadmium halides. It is also found that the computed values of R for the solutions are always higher than the theoretically experimental values. Taking the ratio K of computed to experimental value of R as an index of the degree of association and solvation, these values are plotted against molar fraction C_m as shown in Fig. 7. The value of $K = 1.253$ obtained for zero concentration gives an idea of the degree of association in pure water which is responsible for the lowering of R. In the presence of an electrolyte the water molecules will be dissociated, consequently there will be a decrease in the value of R. Simultaneously there is also the phenomenon of solvation which increases the value of K. In all the acetates studied K decreases with increase of concentration showing a decrease of association of water molecules with concentration. In the case of aqueous solutions of cadmium chloride

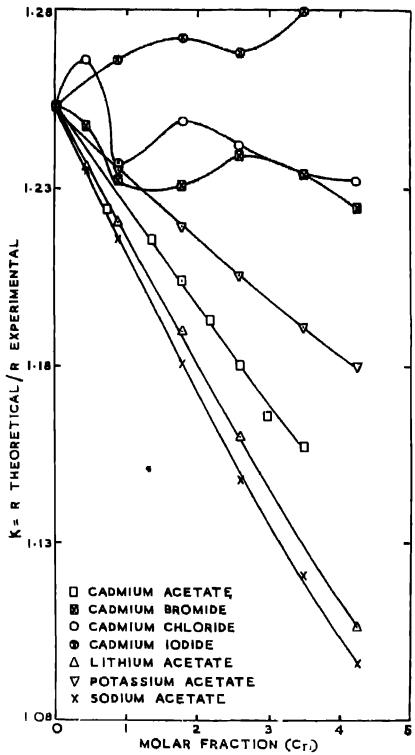

FIG. 7. Variation of "K" factor with molar fraction "C_m"

bromide and iodide peculiar variations of the factor K are observed. The curves show maxima and minima indicating that the process involved is quite complex. This effect is particularly predominant in the case of cadmium iodide for which the K factor continuous to increase with concentration, a feature which is quite unusual.

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